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Using oxygen isotopes to quantitatively assess residual CO₂ saturation during the CO₂CRC Otway Stage 2B Extension residual saturation test

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29 **Abstract**

30 Residual CO₂ trapping is a key mechanism of secure CO₂ storage, an essential
31 component of the Carbon Capture and Storage technology. Estimating the amount of CO₂ that
32 will be residually trapped in a saline aquifer formation remains a significant challenge. Here,
33 we present the first oxygen isotope ratio ($\delta^{18}\text{O}$) measurements from a single-well experiment,
34 the CO₂CRC Otway 2B Extension, used to estimate levels of residual trapping of CO₂.
35 Following the initiation of the drive to residual saturation in the reservoir, reservoir water $\delta^{18}\text{O}$
36 decreased, as predicted from the baseline isotope ratios of water and CO₂, over a time span
37 of only a few days. The isotope shift in the near-wellbore reservoir water is the result of isotope
38 equilibrium exchange between residual CO₂ and water. For the region further away from the
39 well, the isotopic shift in the reservoir water can also be explained by isotopic exchange with
40 mobile CO₂ from ahead of the region driven to residual, or continuous isotopic exchange
41 between water and residual CO₂ during its back-production, complicating the interpretation of
42 the change in reservoir water $\delta^{18}\text{O}$ in terms of residual saturation. A small isotopic distinction
43 of the baseline water and CO₂ $\delta^{18}\text{O}$, together with issues encountered during the field
44 experiment procedure, further prevents the estimation of residual CO₂ saturation levels from
45 oxygen isotope changes without significant uncertainty. The similarity of oxygen isotope-
46 based near-wellbore saturation levels and independent estimates based on pulsed neutron
47 logging indicates the potential of using oxygen isotope as an effective inherent tracer for
48 determining residual saturation on a field scale within a few days.

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50 **Keywords:** residual saturation, oxygen isotopes, Otway, geochemical tracer, CO₂ storage

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1. Introduction

Geological storage of CO₂ in rock formations, as part of Carbon Capture and Storage (CCS), is a promising means of directly lowering CO₂ emissions from fossil fuel combustion (Metz et al., 2005). CO₂ can be stored in the subsurface in three different ways over short timescales: (1) structural trapping, where gaseous or liquid CO₂ is trapped beneath an impermeable cap rock, (2) residual trapping, the immobilisation of CO₂ through trapping within individual and dead end spaces between rock grains, and (3) solubility trapping, where CO₂ is dissolved into the reservoir water that fills the pores between rock grains. Mineral trapping of CO₂ as a result of chemical reactions of the injected CO₂ with the host rock, forming new carbonate minerals within the pores, is a longer term storage mechanism, likely to play a role in siliciclastic formations several hundreds of years after initiation of CO₂ injection (e.g., Audigane et al., 2007; Sterpenich et al., 2009; Xu et al., 2003, 2004; Zhang et al., 2009).

For accurately modelling the long term fate of CO₂ in a commercial-scale CCS project, it is of value to develop an efficient plan to quantitatively assess the amount of structural, residual and solubility trapping at the reservoir scale through a short-term test undertaken in the vicinity of an injection well prior to large-scale injection. Such a test would reduce risk and uncertainty in estimating the storage capacity of a formation and would provide a commercial operator with greater reassurance of the viability of their proposed storage site. This is particularly true for residual trapping of CO₂ which can play a major role for CO₂ plume migration, immobilisation, storage security and reservoir management (Doughty and Pruess, 2004; Ennis-King and Paterson, 2002; Juanes et al., 2006; Krevor et al., 2015; Qi et al., 2009). Despite the important role of residual trapping of CO₂ in commercial-scale CCS projects, there is a current lack of cost-effective and reliable methodologies to estimate the degree of residual trapping on the reservoir scale (Mayer et al., 2015).

Stable isotopes may be highly suitable for assessing the movement and fate of injected CO₂ in the formation since they fingerprint the injected CO₂ rather than being a co-injected

compound like perfluorocarbon tracers, Kr or Xe (Mayer et al., 2013). There are few sources of available oxygen other than the reservoir water within CO₂ storage reservoirs (Johnson et al., 2011; Mayer et al., 2015). Any other reservoir oxygen that is available for water-rock reactions is typically in isotopic equilibrium with the reservoir fluid due to relatively fast reaction kinetics in the water-carbonate system (e.g., Mills and Urey, 1940; Vogel et al., 1970). During CO₂ injection, a new major source of oxygen is added to the system in the form of supercritical CO₂. Isotopic equilibrium exchange proceeds rapidly between oxygen in CO₂ and oxygen in water of various salinities (Kharaka et al., 2006; Lécuyer et al., 2009). In most natural environments the amount of oxygen in CO₂ is negligible compared to the amount of oxygen in water. Consequently, the oxygen isotope ratio ($\delta^{18}\text{O}$) of water remains essentially constant and $\delta^{18}\text{O}$ of CO₂ approaches that of the water plus the appropriate isotopic enrichment factor between water and CO₂ ($\epsilon \approx 10^3 \ln \alpha_{\text{CO}_2\text{-H}_2\text{O}}$), depending on the reservoir temperature (Bottinga, 1968). At CO₂ injection sites, due to the large quantities of CO₂ injected, CO₂ becomes a major oxygen source, and both CO₂ and water will change their $\delta^{18}\text{O}$ due to isotopic equilibrium exchange reactions if the injected CO₂ is isotopically distinct with respect to the baseline reservoir water (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006; Mayer et al., 2015). This has also been observed in natural settings characterised by vast amounts of free-phase CO₂ in contact with water produced from CO₂-rich springs, for example in south east Spain (Céron and Pulido-Bosch, 1999; Céron et al., 1998) or in Bongwana, South Africa (Harris et al., 1997). The change in reservoir water $\delta^{18}\text{O}$ due to isotopic exchange with CO₂ under conditions typical for CO₂ injection sites can be related to the fraction of oxygen in the system sourced from CO₂ (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006), and the fraction of oxygen sourced from CO₂ can be successfully used to assess volumetric saturation of free-phase and dissolved CO₂ in the reservoir (Johnson et al., 2011; Li and Pang, 2015).

CO2CRC Limited (CO2CRC) developed and has operated the CO2CRC Otway Facility in the Otway Basin near Nirranda South, Victoria, Australia, since 2004 (Sharma et al., 2007).

The facility allows for trial injection in multiple storage types, including a saline formation that currently uses a single-well configuration. This configuration is ideal for the development of an effective reservoir characterisation test prior to commercial-scale CO₂ injection (Paterson et al., 2011). In 2011, the first single-well injection test (using the CRC-2 injection well) was undertaken at the Otway facility using 150 t of injected CO₂ to quantify reservoir-scale residual trapping of CO₂ in a saline formation in the absence of an apparent structural closure (CO₂CRC Otway Stage 2B – henceforth referred to as Otway 2B; Paterson et al., 2011, 2013, 2014). The target reservoir for the experiment was within the Paaratte Formation, a saline formation at 1075-1472 m TVDSS (true vertical depth below mean sea level), with the target interval for the Otway 2B experiment at 1392-1399 m TVDSS. Deep saline formations are the most likely candidates for geological CO₂ storage because of their huge potential capacity and their locations close to major CO₂ sources (Holloway, 2001). The Paaratte Formation, while only used for research purposes, is a saline formation analogous to those proposed for commercial-scale CO₂ injection and storage. Two of the original measurements of residual CO₂ saturation were acquired using noble gas (Xe and Kr) tracer injection and recovery data (LaForce et al., 2014), and pulsed neutron logging of the CRC-2 injection well (Schlumberger Residual Saturation Tool; Dance and Paterson, 2016; Paterson et al., 2013, 2014). The second part of the recent CO₂CRC Otway Stage 2B Extension project (henceforth referred to as Otway 2B Extension) was a smaller-scale repeat of these two residual saturation tests using improved methodologies.

Here we present oxygen ($\delta^{18}\text{O}$) and hydrogen isotope ($\delta^2\text{H}$) data from produced water and formation water (U-tube) samples, and oxygen isotope data from CO₂ samples from the Otway 2B Extension. For the first time we estimate levels of residual trapping of CO₂ based on oxygen isotope data from a single-well test. We compare our results with measures from independent techniques to estimate residual saturation.

2. CO2CRC Otway Stage 2B Extension Project

The Otway 2B Extension was conducted in October-December 2014 over a time span of 80 days. The target formation for the Otway 2B experiments, the Paaratte Formation, is a complex interbedded formation of medium to high permeability sandstones and thin carbonaceous mud-rich lithologies, deposited in multiple progradations of delta lobes during the Campanian (Bunch et al., 2012; Dance et al., 2012; Paterson et al., 2013). The target interval for the Otway 2B experiments at 1392-1399 m TVDSS is characterised by well-sorted texturally submature deltaic sandstone dominated by quartz and low clay and feldspar contents, overlain by a diagenetic carbonate seal (Kirste et al., 2014; Paterson et al., 2013, 2014). The sandstone is characterised by a porosity of ~28%, an average permeability of 2.2 Darcy and a fluid salinity of 800 mg/L (Bunch et al., 2012; Dance et al., 2012). The target reservoir is overlain by a cemented interval and a thick non-reservoir lithofacies interval with a high sealing capacity (Paterson et al., 2013, 2014). The CRC-2 well is equipped with a U-tube geochemical sampling system (Freifeld et al., 2005) and a set of four pressure and temperature gauges at the top and bottom of the target interval for the Otway 2B experiments.

The aims of the Otway 2B Extension were to study differences in reservoir water quality in response to the injection of CO₂-saturated water with and without trace amounts of gas impurities (Phase 1), and to characterise the residual trapping levels of CO₂ after injection of pure CO₂ into the formation (Phase 2). Our study primarily focuses on Phase 2. However, to study baseline conditions in the reservoir during the entire project, samples were taken during the initial production of 535.8 t of water from the target interval prior to Phase 1 and during the water injection for Phases 1.1 (days 11-12) and 1.2 (days 35-36), the two push-pull tests characterising Phase 1. Further, samples of produced water from Phases 1.1 (day 35) and 1.2 (days 62-63) were taken. Operational details of Phase 1 are presented in a separate study (Haese et al., in prep.).

Phase 2 started with the production of 75.1 t of water on days 63-64 (Table 1). On day 65, 67 t of previously produced water was injected for the 'water test', together with Kr, Xe and methanol dissolved into the water during the injection (Phase 2.1). Water production with U-tube and production water sampling to study the tracer behaviour at reservoir conditions without CO₂ in the formation commenced immediately after the injection, producing 122.2 t of water on days 65-67. A pulsed neutron log was run on day 68 to provide a baseline for the near-wellbore conditions prior to the drive to residual saturation. This was followed by the injection of 109.8 t of pure CO₂ on days 68-72 (Phase 2.2). Immediately following the CO₂ injection, another pulsed neutron log was run to measure the CO₂ response to test if the near-well saturation was consistent with the predictions. On days 72-74, 323.7 t of previously extracted water, saturated with 17.5 t of CO₂, was injected to drive the reservoir to residual saturation (Phase 2.3). The injected water that drives the reservoir to residual saturation was fully saturated with CO₂ to avoid dissolving the residually trapped CO₂. The near-well saturation was tested using a final pulsed neutron log. On day 75, 67.2 t of previously produced water, now saturated with 3.9 t of CO₂ and containing trace amounts of Kr, Xe and methanol, was injected, followed by production of 128.5 t of water with U-tube and water sampling over three days. This allowed measurement of the tracer partitioning between water and residually trapped CO₂ in the reservoir during the 'residual saturation test' (Phase 2.4). Finally, the excess water remaining in the surface tanks was re-injected for disposal on days 78-80. Downhole temperatures and pressures were recorded through the entire duration of the project. The injected gas for the Otway 2B Extension was a mix of industrial CO₂ captured at the Callide Oxyfuel pilot capture plant in Queensland (Callide CO₂) and food grade CO₂ (99.9 %) from the Boggy Creek well in the vicinity of the Otway site (BOC CO₂).

3. Materials and Methods

3.1 Materials

Water and gas samples were collected using the U-tube system (Freifeld et al., 2005). This system provides the advantage of collecting reservoir water at in situ reservoir pressure of ~140 bar, so that the dissolved gas does not exsolve during the ascent of the sample fluid from the reservoir. At Otway, pressurised water samples were collected in 150 mL stainless steel Swagelok cylinders with needle valves on each end. The cylinder was connected to either a 1 L, 5 L or 10 L Restek™ multi-layer gas bag with a polypropylene combo valve, depending on the amount of gas expected. The cylinder was depressurised under controlled conditions for approximately one hour to collect all of the produced CO₂ and other gases in the gas bag. Wet chemical analyses including pH, alkalinity, electrical conductivity and salinity were conducted on the produced water samples in the purpose-built field laboratory. After processing the water samples in the field laboratory, the depressurised fluids were filtered to 0.45 µm and ~8 mL of the filtered fluid transferred into a 10 mL pre-evacuated BD® plastic vacutainer through the self-sealing lid of the vacutainer using a hypodermic needle for subsequent isotope analysis.

Injection waters were sampled downstream of the oxygen scavenger (see Paterson et al., 2011, for a detailed description and illustration of the CRC-2 process flow setup). Production waters in addition to U-tube samples were sampled directly from the production water line after the degassing tank. The injection and production water samples were filtered to 0.45 µm and transferred to 60 mL Nalgene bottles with tight fitting caps, with zero headspace on filling to prevent evaporation.

A sample of the pure CO₂ gas from the nearby Boggy Creek production well (BOC CO₂) was collected for stable isotope analyses in a 1 L gas bag directly from the BOC tanker. Duplicate samples of the Callide industrial CO₂ were collected for isotopic analyses by depressurising a 150 mL stainless steel Swagelok cylinder containing liquid CO₂ filled directly from the Callide tanker.

3.2 Methods

Water and CO₂ samples were analysed at the Stable Isotope Geochemistry Laboratory at the School of Earth Sciences of the University of Queensland, Australia. Water samples were analysed for oxygen isotopes after standard CO₂ equilibration (Epstein and Mayeda, 1953) and for hydrogen isotopes after online equilibration at 40 °C with Hokko coils, using an Isoprime Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) coupled to a Multiprep Bench for online analysis. Delta values in water samples are reported in ‰ deviation relative to VSMOW (Vienna Standard Mean Ocean Water) for both oxygen and hydrogen isotopes according to

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

where R represents the ¹⁸O/¹⁶O and ²H/¹H ratios of samples and standards, respectively. Analytical uncertainties for water δ²H and δ¹⁸O are ±2 ‰ (1σ – one standard deviation) and ±0.1 ‰ (1σ), respectively. All laboratory standards were calibrated against IAEA (VSMOW, SLAP, GISP) and USGS (USGS45, USGS46) international water standards.

CO₂ samples were analysed using an Isoprime/Agilent Gas Chromatograph-combustion-Isotope Ratio Mass Spectrometer (GC-c-IRMS). All samples were analysed using a 20:1 split. The gas chromatograph (GC) (with a 50 m × 320 μm × 5 μm CP-PoraBOND Q column) was set to a flow of 1.2 mL/min with an oven temperature of 40 °C. The δ¹⁸O values of the CO₂ gas (reported in ‰; δ¹⁸O_{CO₂}) were normalised to the VSMOW scale following a 2-point normalisation (Paul et al., 2007). NBS18 and NBS19 international reference standards were analysed to confirm calibration of the δ¹⁸O scale. The analytical uncertainty for δ¹⁸O in gas samples is ±0.2 ‰ (1σ).

4. Results

4.1 Hydrogen isotopes in water samples

Values of $\delta^2\text{H}$ in water samples remain relatively constant throughout the entire Otway 2B Extension (Fig. 1). All samples bar one of the duplicate samples from the initial water production prior to Phase 1.1 and the first water sample from the CO_2 -saturated water injection of Phase 1.1 fall within the 1σ range ($\pm 1.78\text{‰}$) of the average of all samples from the entire Otway 2B Extension (-30.19‰ ; excluding the duplicate sample with much higher values from the initial water production). Four water samples were collected from the injection water during Phase 1.1, and the average of the four ($-33.58 \pm 1.00\text{‰}$) is marginally outside of the 1σ range of the average from all samples. Values of reservoir water $\delta^2\text{H}$ throughout the Otway 2B Extension are similar to baseline reservoir water values during the previous Otway 2B experiment in 2011 (~ -25 to -33‰ ; Kirste et al., 2014). The water $\delta^2\text{H}$ of samples collected directly from the production line into bottles and samples from the U-tube during both the water and residual saturation tests show an excellent correlation within their analytical uncertainties.

4.2 Oxygen isotopes in water samples

For reservoir water $\delta^{18}\text{O}$, almost all samples prior to the three days of water production for Phase 2.4 fall in the 1σ range (0.19‰) of the average of these bottle and U-tube samples (-6.01‰) (Fig. 2). This baseline value is similar to the values for the first Otway 2B experiment in 2011 of around -5 to -6‰ (Kirste et al., 2014). Only the two samples of injection water for Phase 1.2 ($\delta^{18}\text{O}$ of ~ -5.6 to -5.7‰) as well as two samples from the water production prior to Phase 2.1 ($\delta^{18}\text{O}$ of $\sim -6.4\text{‰}$) fall outside of the 1σ range. During the three days of water production for Phase 2.4 (days 75-77), when water samples in contact with CO_2 in the reservoir were collected, a decrease was observed in $\delta^{18}\text{O}$ ratios of reservoir water in both the

bottle and U-tube samples to the lowest values recorded throughout the experiment of $-6.63 \pm 0.10 \text{ ‰}$ and $-6.46 \pm 0.10 \text{ ‰}$, respectively. This indicates a shift away from stable baseline conditions without CO₂ prior to Phase 2.4 (Fig. 2 and 3). In particular, the $\delta^{18}\text{O}$ values of both the bottle and U-tube samples from the last day of water production are clearly lower compared to the baseline conditions, while $\delta^2\text{H}$ values remain constant throughout the entire project (Fig. 3).

In contrast to $\delta^2\text{H}$, there is an offset between $\delta^{18}\text{O}$ values in water samples from bottles and the U-tube for the water and residual saturation tests (Fig. 2). Bottle samples have consistently lower $\delta^{18}\text{O}$ values compared to the U-tube samples, although the offset is not constant from sample to sample.

5. Discussion

5.1 Baseline Stable Isotope Conditions and Small-Scale Baseline Changes Prior to CO₂ Injection

Concurrently increasing or decreasing final water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$) and $\delta^2\text{H}$ values of reservoir water compared to baseline values can indicate admixture of different waters with variable isotopic compositions, while a change in $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$ without any change in $\delta^2\text{H}$ suggests water-CO₂ interaction in the reservoir when mineral dissolution can be excluded (e.g., D'Amore and Panichi, 1985; Johnson and Mayer, 2011; Johnson et al., 2011). Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of reservoir water prior to CO₂ injection remained relatively stable during these “baseline” conditions, with $\delta^2\text{H}$ of reservoir water showing no change from the stable baseline conditions during the entire Otway 2B Extension (Fig. 1 and 2). This provides strong evidence for no major evaporation or water mixing processes at surface or in the reservoir. Further, both $\delta^{18}\text{O}$

and $\delta^2\text{H}$ show similar baseline conditions compared to the 2011 Otway 2B experiment, indicating that any free-phase CO_2 potentially remaining in the reservoir near the well at the end of the previous Otway 2B experiment dissolved and only negligibly changed the $\delta^{18}\text{O}$ signature of the reservoir water between the end of the first and initiation of the second Otway 2B experiment.

This is also supported by numerical simulations that have been run to investigate the distribution of fluids in the reservoir at the start of the Otway Stage 2B Extension. Detailed geological data were used to construct a near-well radial grid for the reservoir unit, and the complete sequence of production and injection of fluids from 2011 onwards, including tracers, was simulated using the TOUGH2 simulator with the EOS7G equation of state module, which can model methane, CO_2 and tracers. The simulations were matched against the relevant field data for pressure, temperature and produced concentrations in the 2011 Otway Stage 2B experiment, so this gives some confidence that the model accurately represents the reservoir behaviour during the 2011 test and beyond. The details of these simulations will be reported elsewhere. By running the model forward from the end of 2011 data, the prediction was that at the beginning of the 2014 experiment, the free-phase CO_2 had been dissolved from the immediate vicinity of the well. Any remaining free-phase CO_2 was predicted to be confined to a thin layer at the top of the reservoir unit, and away from the well.

We collected two U-tube samples in duplicate from the initial water production prior to Phase 1.1, and one of these duplicate samples shows higher $\delta^2\text{H}$ values compared to the other U-tube sample collected just prior (Fig. 1). The oxygen isotope composition of the duplicates of both initial water production samples is very similar and within the range of all water samples collected prior to CO_2 injection during Phase 2 (Fig. 2). Since these two samples from the initial water production were stored over six months in a refrigerator in a Falcon tube with around 20 % cap space prior to analysis, and since both samples were collected consecutively and one of the samples shows $\delta^2\text{H}$ values in accordance with the other collected samples during the project (Fig. 1), the higher $\delta^2\text{H}$ values of one of the initial water

production samples can potentially be explained by storage contamination influencing only hydrogen isotopes.

Only four samples fall outside of the 1σ range of the average of all samples prior to the production phase of the residual saturation test for $\delta^{18}\text{O}$: the two samples of injection water for Phase 1.2 and two samples from the water production prior to the water test. The injection water for Phase 1.2, derived from a different surface storage tank as the water injected during Phase 1.1, shows both slightly higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compared to the water injected into the formation around one month earlier during Phase 1.1 (Fig. 1 and 2), potentially indicating minor evaporation processes and/or oxygenation of water in the surface storage tanks (Haese et al., in prep.). At the end of the water production prior to Phase 2.1, more water (212.3 t) was produced than injected during Phases 1.1 and 1.2 (202.2 t). Therefore, it is possible that the last few tons of the water produced was either older reservoir water from prior to the Otway 2B Extension or a mixture of this considerably older reservoir water with injected water from Phase 1. This could explain the lower $\delta^{18}\text{O}$ of the waters produced on the day before Phase 2.1.

The stability of reservoir water $\delta^{18}\text{O}$ prior to Phase 2.4 provides evidence that, with the exceptions noted above, $\delta^{18}\text{O}$ remained stable during baseline conditions when reservoir water was not in contact with free-phase CO_2 . During the three days of water production of Phase 2.4, a decrease in $\delta^{18}\text{O}$ of water in contact with free-phase CO_2 in the reservoir occurred, indicating a clear shift from the stable baseline conditions (Fig. 2 and 3). This change in water $\delta^{18}\text{O}$ can be used in the following to estimate the fraction of CO_2 that is residually trapped in the reservoir.

5.2 Estimation of Residual CO_2 Saturation Based on Oxygen Isotope Values of Reservoir Water

The method used here to estimate residual CO₂ saturation based on changes in δ¹⁸O of reservoir water in contact with free-phase CO₂ is described in detail in Johnson et al. (2011). If the majority of oxygen in the system is sourced from CO₂, as is the case near the injection well after Phase 2.3, δ¹⁸O_{CO₂} will dominate the water-CO₂ system. The δ¹⁸O ratio of reservoir water will start to change from the baseline water oxygen isotope value, δ¹⁸O_{H₂O}^b, towards an end-member scenario where the water has a final water value δ¹⁸O_{H₂O}^f lower than that of the injected CO₂ by the isotopic enrichment factor (Johnson et al., 2011). In this case, the fraction of oxygen in the system sourced from CO₂, X_{CO₂}^o, can be estimated using

$$X_{CO_2}^o = \frac{(\delta^{18}O_{H_2O}^b - \delta^{18}O_{H_2O}^f)}{(\delta^{18}O_{H_2O}^b + \epsilon - \delta^{18}O_{CO_2})} \quad (2)$$

The isotopic enrichment factor ε between CO₂ and water is reported in ‰ and determined using the equation defined by Bottinga (1968)

$$\epsilon = -0.0206 \times \left(\frac{10^6}{T^2}\right) + 17.9942 \times \left(\frac{10^3}{T}\right) - 19.97 \quad (3)$$

where T is the reservoir temperature in Kelvin. This equation is valid at atmospheric conditions as well as elevated temperatures and pressures relevant for CCS projects (Becker et al., 2015; Bottinga, 1968; Johnson et al., 2011).

The water-CO₂ system for oxygen in a reservoir can be described quantitatively in terms of the averaged reservoir CO₂ saturation for the region contacted by CO₂ and measured with the water sample (S_{CO₂}) using

$$S_{CO_2} = \frac{(BX_{CO_2}^o + CX_{CO_2}^o - B)}{(A - B - AX_{CO_2}^o + BX_{CO_2}^o + CX_{CO_2}^o)} \quad (4)$$

with A referring to moles of oxygen in 1 L of free-phase CO₂ at reservoir conditions, B to moles of oxygen dissolved in 1 L water from CO₂ at reservoir conditions, and C to moles of

oxygen in 1 L water at reservoir conditions (Johnson et al., 2011). During Phase 2.3, the injection of CO₂ and water generally matched the target ratio during most of the water injection for the drive to residual. However, late during the injection, there were periods of delivery of added CO₂ below the target, potentially resulting in some dissolution of residually trapped CO₂ near the wellbore. Thus, in this experiment estimates of S_{CO₂} based on oxygen isotopes provide flow-weighted averages of CO₂ saturation, and we expect that S_{CO₂} levels in the reservoir are variable over distance from the borehole, with lower saturation estimates near the wellbore.

Eq. (4) was first applied during the enhanced oil recovery (EOR) Pembina Cardium CO₂ monitoring project in Alberta, Canada, to estimate S_{CO₂} (Johnson et al., 2011), and the robustness of this approach has been validated using laboratory (Barth et al., 2015; Johnson and Mayer, 2011) and theoretical studies (Li and Pang, 2015). It has been further shown by Johnson et al. (2011) that the method outlined above provides S_{CO₂} estimates from the Frio experiment in east Texas (USA) similar to estimates from an approach that did not assume established isotopic equilibrium between water and CO₂ and that uses volumetric ratios of water and CO₂ determined from known changes in water and CO₂ δ¹⁸O (Kharaka et al., 2006). The method can only be applied if isotopic exchange with minerals in the reservoir can be excluded. Injected CO₂ may form carbonic acid and liberate oxygen from the minerals in the reservoir, e.g. through calcite dissolution (Gunter et al., 1993). Based on detailed analyses of all major and minor cations and anions indicating fluid-mineral reactions, including Si, Al, Ca, Mg, K and HCO₃⁻, in reservoir water samples collected during Phase 1 (Haese et al., in prep.), silicate mineral dissolution can be ruled out. Very minor carbonate mineral (calcite and siderite) dissolution was observed. However, the amount of oxygen liberated from carbonate will be very small compared to the total oxygen from CO₂ and water. Sterpenich et al. (2009) demonstrated that less than 1% by mass of an oolitic limestone dissolved due to interaction with CO₂-saturated water under experimental conditions (150 bar, 80 °C) at water-rock ratios 40 times higher than those typical for reservoirs considered for CO₂ injection. Further, since

the target interval of the reservoir is characterised by deltaic sandstones dominated by quartz and low clay and feldspar contents (Kirste et al., 2014; Paterson et al., 2013, 2014), any contribution of oxygen from dissolution of carbonate minerals to the total oxygen inventory in the target interval is negligible. Therefore, we conclude that we can eliminate isotopic exchange with minerals as a contribution to oxygen isotope changes in the reservoir water during the Otway 2B Extension.

As mentioned above, we observe an offset between $\delta^{18}\text{O}$ values in water samples collected directly from the production line and U-tube samples during the water and residual saturation tests, with lower $\delta^{18}\text{O}$ values in bottle compared to U-tube samples, while no change can be observed in $\delta^2\text{H}$ (Fig. 1 and 2). The isotopic equilibrium between water and injected CO_2 is established before CO_2 exsolves (Johnson et al., 2011). Consequently, the U-tube fluid, which is the formation fluid depressurised at atmospheric pressure and therefore not in contact with the atmosphere or reservoir gas over longer time scales, provides our best estimate of $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$ in the reservoir at the time of sampling. Consequently, we use the U-tube sample values to estimate CO_2 saturation in the following.

5.3 Uncertainties in Water and CO_2 Source Mixing

5.3.1 Water Baselines and Production

For the approach to estimate residual CO_2 saturation outlined above to be robust, it is essential to have a reliable baseline $\delta^{18}\text{O}$ for reservoir water. A total of 390.9 t of CO_2 -saturated water was injected during Phases 2.3 (323.7 t) and 2.4 (67.2 t) prior to producing 128.5 t of water in Phase 2.4 (days 75-77). Consequently, we expect that the water produced in Phase 2.4 was a mixture of the injection water of Phases 2.3 and 2.4. The 323.7 t of CO_2 -saturated water injected during Phase 2.3 (days 72-74) had an average water $\delta^{18}\text{O}$ of $-6.07 \pm 0.07 \text{ ‰}$ and $\delta^{18}\text{O}_{\text{CO}_2}$ of $+27.65 \pm 0.12 \text{ ‰}$ for the co-injected CO_2 , resulting in a $\delta^{18}\text{O}$ value for the fully

CO₂-saturated water of -6.18 ± 0.07 ‰ at wellbore conditions. On day 75, 67.2 t of CO₂-saturated water containing noble gas tracers were injected for Phase 2.4, with an average water $\delta^{18}\text{O}$ of -5.79 ± 0.07 ‰ and $\delta^{18}\text{O}_{\text{CO}_2}$ of $+29.30 \pm 0.20$ ‰ for the co-injected CO₂, resulting in a $\delta^{18}\text{O}$ value for the fully CO₂-saturated water of -5.86 ± 0.07 ‰ at wellbore conditions.

The Phase 2.3 (first) injection of CO₂-saturated water thus has a slightly different oxygen isotope signature compared to the injection water for Phase 2.4, resulting in the necessity to account for mixing of these two water masses in the reservoir to provide a reliable baseline value for the estimation of residual saturation on each of the three days of water production. We used the data on co-injected methanol to estimate the mixing ratio of the two water masses during the water production stage. Methanol is a non-reactive tracer that can be applied to study mixing of water masses in a reservoir (e.g., Haese et al., 2013; Tomich et al., 1973). The methanol concentration of the injected water in Phase 2.4 was 330 ± 20 ppm based on duplicate samples from the injection line, and three U-tube samples collected during injection. Methanol was measured in nearly all U-tube samples collected during the water production stage of Phase 2.4. The injected water for Phase 2.3 was sourced from two different water storage tanks, with the last 111 t of the water sourced from the same tank used for the water injection and production during Phase 2.1 (Tank 3), and therefore containing methanol. The other 212 t of the injection were sourced from another tank (Tank 2) containing low levels of methanol (around 25 ppm by mass). Mass balance calculations suggest that the methanol concentration in Tank 3 should have been around 130 ppm at the start of Phase 2.3. Two U-tube samples taken after the Phase 2.3 injection gave an average methanol concentration in the reservoir of 87.5 ppm, suggesting that the injection concentration may have been slightly less than the mass balance calculation would suggest.

Fig. 4 shows the U-tube data for the concentration of methanol in the back-produced water in Phase 2.4, with the horizontal axis normalised as the produced volume relative to the injected volume (67.2 t). If there was no mixing between the two masses of injected water,

then one would expect this to be a step function, but there is obviously a degree of mixing, and this is determined by the hydrodynamic dispersion of the reservoir unit around the well.

A simple theoretical result can be obtained for the effect of longitudinal dispersion on the injection of a uniform tracer into a homogeneous reservoir with no initial tracer (Gelhar and Collins, 1971; Güven et al., 1985), and trivially modified for the case of a uniform background concentration of tracer already in the reservoir. Let C be the concentration of the tracer in the produced fluid, C_0 the injected tracer concentration, and C_b the uniform concentration of tracer already in the reservoir. Let x be the ratio of the cumulative volume of produced fluid at any time to the volume of the original injected fluid. The ratio of radial dispersivity α to the radial penetration depth of the tracer, R , is b . If the reservoir is perfectly stratified, and only longitudinal dispersion is considered, then

$$C = (C_0 - C_b) \frac{1}{2} \operatorname{Erfc} \left(\frac{(x-1)}{\left(\frac{16b}{3} \left(2 - |1-x|^{\frac{1}{2}} (1-x) \right) \right)^{1/2}} \right) + C_b \quad (5)$$

In our case, it is only the last 111 t of water injected in Phase 2.3 that contain the tracer concentration C_b . After the injection of 67.2 t in Phase 2.4, the last part of the back-production of 128.5 t will probably not be producing water beyond that 111 t, so we can consider the tracer concentration in the reservoir to be uniform. If the theoretical result is fit to the methanol data by varying C_0 , C_b and b then the curve in Fig. 4 is obtained. The fitted value of C_0 is 331 ppm (with a standard error of 7.2 ppm), which agrees well with the measured concentration of injected methanol. The fitted value of C_b is 98.6 ppm (with a standard error of 8.7 ppm), which is close to the measured concentration in the reservoir before the Phase 2.4 injection. The parameter b has a fitted value of 0.0177 (with a standard error of 0.0055). Numerical simulations indicate that the average radial penetration depth R of the tracer is about 3.5-3.8 m, so the fitted radial dispersivity α is 0.062 to 0.067 m.

The quality of the fit is worst during the early back-production, and this matches with observations made in other similar continuous injection tracer tests (Güven et al., 1985). Hydrodynamic dispersion acts to smooth out tracer concentrations, and since the tracer that was first produced was that last injected (and which has been subject to the least dispersion), this may explain some of the initial scatter in the tracer concentrations.

The theory can be extended to take account of permeability contrasts between layers, but for the current test the corresponding result was barely different to the homogeneous case with averaged properties, and so the calculations are not detailed here. Vertical dispersivity has been ignored, although for larger injections into heterogeneous reservoirs this can cause a much longer tail in the back-production, as the tracer disperses from the high permeability layers into the low permeability ones.

The fitted analytical theory then gives a straightforward means of estimating the degree of mixing in the reservoir, and the results are summarised in Table 2, where the range of the prediction is obtained by varying the parameter b within the range of the standard error.

5.3.2 CO₂ Source

A potential uncertainty in the estimation of residual CO₂ saturation using oxygen isotopes can further result from the mixing of CO₂ from two different sources in the reservoir. The first 12.2 t of the 109.8 t of pure CO₂ injected and residually trapped in the reservoir were Callide CO₂ with a $\delta^{18}\text{O}$ ratio of $+26.05 \pm 0.14$ ‰, while the remaining 97.6 t of pure CO₂ was BOC CO₂ with an oxygen isotope signature of $+29.30 \pm 0.20$ ‰. For the following estimation of residual CO₂ saturation, we assumed perfect mixing of these two CO₂ sources in the reservoir and derived the $\delta^{18}\text{O}_{\text{CO}_2}$ ratio to be used in Eq. (2) as a weighted average based on the amounts of the two injected CO₂ sources. This results in a $\delta^{18}\text{O}_{\text{CO}_2}$ ratio for the residually trapped CO₂ of $+28.94 \pm 0.12$ ‰. We consider this approach as the most reliable to assess

$\delta^{18}\text{O}_{\text{CO}_2}$ since we do not have an estimate for the mixing of CO_2 in the reservoir or of variable oxygen isotope signatures of CO_2 in contact with water in the reservoir.

5.4 Estimates of Residual CO_2 Saturation in the Paaratte Formation

For each U-tube sample collected for stable isotopes during the three days of water production, we used Eqs. (2)-(4) to estimate residual trapping levels. We used the thermodynamic model of Duan and Sun (2003) to derive solubilities and densities of CO_2 in aqueous NaCl solutions under wellbore conditions for each individual day since temperatures and pressures varied throughout the experiment (Table 3). As mentioned above, the average wellbore temperatures and pressures for the times of U-tube sample collection were derived from the four temperature and pressure gauges in the perforated interval

The first water production sample was collected ~7 hours after the start of water production and ~9 hours after the end of CO_2 -saturated water injection. With an isotopic enrichment factor of 36.84 ‰ based on Eq. (3) and a $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+28.94 \pm 0.12$ ‰, we expect the reservoir water in contact with free-phase CO_2 in the reservoir to change to lower $\delta^{18}\text{O}$ values compared to the assumed $\delta^{18}\text{O}_{\text{H}_2\text{O}}^b$ value if isotopic equilibrium exchange between reservoir water and CO_2 is established [Eq. (2)]. Our approach provides a value for $X_{\text{CO}_2}^0$ of 0.13 ± 0.06 (Table 4). This indicates that enough oxygen sourced from CO_2 was available in the reservoir to change the oxygen isotope signature of the reservoir water after only a few hours. The $X_{\text{CO}_2}^0$ value provides a residual saturation estimate based on oxygen isotopes of 14 ± 9 % [Eq. (4)].

For the second sample collected on day 76 with a $\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$ value of -6.27 ± 0.10 ‰, the methanol approach indicates that 22 ± 8 % of the oxygen in the water- CO_2 system is sourced from the residually trapped CO_2 , which results in a residual saturation estimate of 28 ± 11 %

(Table 4). The sample collected on the last day of Phase 2.4 (day 77) has the lowest $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$ value of all samples collected, with $-6.46 \pm 0.10 \text{ ‰}$, and is clearly distinct from the baseline water $\delta^{18}\text{O}$ prior to the injection of free-phase CO_2 ($-6.01 \pm 0.19 \text{ ‰}$) (Fig. 2 and 3). Our approach provides an $X_{\text{CO}_2}^{\text{O}}$ estimate of $32 \pm 13 \%$ (Table 4). This results in a residual saturation estimate in the target interval of $42 \pm 16 \%$. Our data do not provide information about the timing of established final isotopic equilibrium between oxygen in water and CO_2 in the reservoir, with previous laboratory studies showing that final isotopic equilibrium at reservoir conditions normally encountered during CCS projects (up to 190 bar and 90 °C) is reached within a one-week period (Becker et al., 2015; Johnson and Mayer, 2011).

While our oxygen isotope data from reservoir water show a clear shift as a result of water- CO_2 isotopic exchange in the reservoir within a few days, our estimates of residual CO_2 saturation are characterised by relatively large uncertainties. Several factors can result in uncertainties in the oxygen isotope approach. First, and most importantly, the oxygen isotopic distinction between the injected CO_2 and baseline reservoir water in consideration of the isotopic enrichment factor at wellbore conditions is relatively small during the Otway 2B Extension. While a predictable $\delta^{18}\text{O}$ shift to lower values in reservoir water in contact with free-phase CO_2 compared to baseline conditions was observed, the small isotopic distinction of the two main oxygen sources resulted in a small isotopic shift in the short time of the Otway 2B Extension and a large uncertainty in S_{CO_2} estimates. Second, there are uncertainties resulting from the field experiment procedure and setup due to variable reservoir conditions during the entire project and uncertainty in the mixing ratios of water masses and CO_2 sources with different isotopic signatures. These uncertainties result in the necessity to make assumptions about mixing ratios of gases and water masses in the reservoir, and about average reservoir conditions during the different phases. The wellbore conditions during the Otway 2B Extension were slightly different compared to the reservoir conditions; in particular, injection temperatures were lower compared to reservoir temperatures ($\sim 59 \text{ °C}$; Bunch et al., 2012; Dance et al., 2012). Since it is uncertain at which exact temperature the isotopic

exchange reactions between free-phase CO₂ and brine occurred in the reservoir, the difference in injection versus reservoir temperature presents an uncertainty in the estimation of residual CO₂ saturation. All these factors can result in larger uncertainties than ideal in the baseline values of CO₂ and reservoir water, and the isotopic enrichment factors assumed for the reservoir.

5.5 Comparison of Independent Estimates of Residual CO₂ Saturation

We can compare our residual S_{CO₂} results from the three days of water production to independent estimates of residual CO₂ saturation in the Otway 2B target interval based on noble gas tracers and pulsed neutron logging from the first Otway 2B experiment. For the comparison of results from the two Otway 2B field experiments, we have to consider that differences in residual saturation levels between the two experiments can result from differences in the timing in events, especially during the water flood.

All three techniques to be compared measure a spatially varying residual saturation over different depths of investigation using different forms of averaging, and are characterised by specific uncertainties and limitations that have to be considered when comparing the results. Pulsed neutron logging provides residual CO₂ saturation levels in the vicinity of the well (~25 cm) at the point of time it is carried out (Adolph et al., 1994; Dance and Paterson, 2016). The CO₂ in the pulsed neutron logging may or may not be residually trapped, using the strict definition of a core test. Pulsed neutron logging and core flooding experiments have further provided evidence that there is a range of residual trapping values throughout a region contacted by CO₂, explained by the Land trapping model (Land, 1968). In this model, the final residual saturation is a function of the maximum CO₂ saturation, and the maximum CO₂ saturation varies throughout the region contacted by CO₂ (e.g., Dance and Paterson, 2016; Krevor et al., 2012, 2015; Land, 1968).

Tracer tests measure the CO₂ saturation achieved after the drive to residual, and provide a flow-weighted average of residual saturation on a larger reservoir scale compared to pulsed neutron logging, similar to oxygen isotopes. Therefore, the tracer data provide an estimate of residual CO₂ saturation for a larger reservoir rock volume characterised by residually trapped CO₂ and reservoir water (LaForce et al., 2014). The results based on numerical simulations of the noble gas data from the first Otway 2B experiment are potentially prone to uncertainties due to the consideration of a noble gas partitioning coefficients based on noble gas-water experiments at low pressures (Fernández-Prini et al., 2003), while recently new noble gas partitioning coefficients in a supercritical CO₂-water system at reservoir conditions became available and show differences to the previously published ones for low-pressure systems (e.g., Warr et al., 2015).

Given the discussed uncertainties and limitations of the techniques, we can now compare the estimates based on oxygen isotope changes in reservoir water with the independent reconstructions of residual CO₂ saturation. The stable isotope sample collected just 7 hours after the start of water production provides a near-wellbore estimate of residual trapping of CO₂, and can therefore be best compared to measures based on pulsed neutron logging. Saturation profiles from the first Otway 2B experiment from pulsed neutron logging show an average residual saturation of 20 %, with an overall range of 7 to 32 % (Dance and Paterson, 2016). While we have to consider the possibility that the water sampled just 7 hours into the water production phase may not have achieved full isotopic equilibrium with residual CO₂ in the reservoir, our estimate for this first stable isotope sample of 14 ± 9 % is similar with the saturation level reconstructed from pulsed neutron logging. The stable isotope sample from the second and third day can be best compared to the estimates based on noble gas injection and recovery. Reconstructed residual CO₂ saturation levels from the multiphase flow simulations of noble gas injection and recovery are between 11 and 20 % for the first Otway 2B experiment (LaForce et al., 2014). These estimates fall in the range of possible S_{CO₂} values based on stable isotopes from the second day (28 ± 11 %), but are lower than the results from

the last day of the Phase 2.4 water production stage ($42 \pm 16 \%$). This trend of increasing S_{CO_2} with distance from the wellbore based on the oxygen isotope shift in the reservoir water is different to the spatial residual trapping distribution in the reservoir from numerical reservoir simulations, which predict decreasing gas saturation with distance from the well, with residuals not exceeding 20 % further from the injection well.

Three potential mechanisms can explain the reconstructed change in oxygen isotopes in the reservoir water during the three days of water production of Phase 2.4. The observed trend can be the result of (1) a higher residual further away from the wellbore that is not reconstructed using the noble gas injection and recovery method, (2) contact of the produced water from the last day of Phase 2.4 with the region of mobile CO_2 ahead of the region driven to residual, and/or (3) higher residual saturation levels reconstructed from oxygen isotopes in waters longer in contact with residually trapped CO_2 in different regions of the reservoir. The region that has been driven to residual does not extend very far into the reservoir and mobile CO_2 from further out may have been pulled towards the well during production. Therefore, mechanism (2) could explain the high S_{CO_2} value reconstructed from the water sampled during the last day of Phase 2.4, but not the higher residual saturation estimate from the second day compared to the first day of water production during Phase 2.4. Mechanism (3) considers alteration of the isotopic values of reservoir water during the back-production that might complicate the interpretation of the oxygen isotope changes in terms of residual saturation in the reservoir. The oxygen isotope shift in the reservoir water away from baseline values may be simply due to the variable CO_2 volumes the waters were in contact with in the reservoir, with water samples characterised by a longer residence time in the supercritical CO_2 -water system from the beginning to end of the production phase. During the back-production of Phase 2.4, the water may have continued exchanging oxygen with residual CO_2 with variable isotopic signatures in the different regions of the reservoir, resulting in further perturbation of $\delta^{18}O_{H_2O}^f$. Since residual CO_2 in the different regions of the reservoir may have already been in contact with other waters and has variable oxygen isotope values compared to the initially

612 injected $\delta^{18}\text{O}_{\text{CO}_2}$ value, and since it is uncertain if there was enough time for continuous
613 isotopic equilibrium exchange of reservoir water on its way to the well during back-production,
614 it is difficult to resolve the potential contribution of mechanism (3) with confidence. Therefore,
615 we cannot estimate the effect of this mechanism for the observed changes in oxygen isotopes
616 of the reservoir water during the experiment.

617 Consequently, we are left with three potential mechanisms to explain the observed
618 oxygen isotope shift in reservoir waters during the residual saturation test, particularly further
619 away from the well. Future modelling and laboratory efforts to study the behaviour of oxygen
620 isotopes in the Paaratte Formation at reservoir conditions, considering timing of injection and
621 production events similar to Stage 2 of the Otway 2B Extension, would help to test our
622 observation of variable residual trapping distribution in the reservoir, and could help further
623 exploring the validity of mechanisms (2) or (3). Until then, all three potential reasons have to
624 be considered in the interpretation of the oxygen isotope shift during the three days of water
625 production, and the true nature of the residual saturation distribution further away from the
626 well remains uncertain. However, mechanisms (2) and (3) are improbable to explain the
627 observed oxygen isotope shift from baseline values for the first stable isotope sample collected
628 shortly after the start of back-production. Therefore, this first water sample is the most reliable
629 of the water production samples in terms of reconstructing residual trapping of CO_2 in the
630 formation. Since the reconstructed residual saturation based on oxygen isotopes from this
631 sample is similar to near-wellbore residual saturation values based on pulsed neutron logging,
632 oxygen isotopes during the Otway 2B Extension show potential as an inherent tracer for
633 residual saturation in a single-well experiment that should be further explored in future field
634 and laboratory experiments.

637 **6. Conclusions and Future Prospect**

Field experiments at EOR sites in Texas (Frio experiment) and Alberta (Pembina Cardium CO₂ monitoring project) provide evidence for the viability of using oxygen isotopes measured in reservoir water and CO₂ to estimate S_{CO_2} over timescales longer than one week (Johnson et al., 2011; Kharaka et al., 2006). This is a parameter that has been difficult to assess using previous monitoring techniques but one which is crucial for determining the efficiency of a CO₂ storage site. The application of oxygen isotopes has further been supported by laboratory rock core experiments (Barth et al., 2015; Johnson and Mayer, 2011), water data from CO₂-rich springs (e.g., Ceron and Pulido-Bosch, 1999; Ceron et al., 1998; Harris et al., 1997), and theoretical studies (Li and Pang, 2015). Our study is the first to provide evidence for a shift in oxygen isotope ratios of reservoir water due to isotopic equilibrium exchange with free-phase CO₂ in a reservoir over only a few days, compared to stable baseline water values prior to CO₂ injection (Fig. 2 and 3).

During Phase 2 of the Otway 2B Extension, the reservoir was characterised by residually trapped CO₂ and fully CO₂-saturated reservoir water. In this setup, oxygen isotope changes in the reservoir water can be used to estimate flow-weighted averages of residual CO₂ saturation. Our data provide residual trapping levels for reservoir rock volumes at different distances from the wellbore. The other techniques used to study residual trapping during the first Otway 2B experiment, noble gas tracers and pulsed neutron logging, are variable in their spatial distribution of reconstructed trapping levels and have different depths of investigation in the reservoir. The estimates of residual saturation based on oxygen isotopes from the different days of water production indicate an increase in residual trapping levels with distance from the wellbore. This trend of increasing residual saturation with distance from the wellbore is not consistent with reservoir simulations, which predict the opposite trend. We show that there are three potential mechanisms to explain the observed oxygen isotope shift from baseline values for the water samples further away from the wellbore, resulting in considerable uncertainty about the true residual saturation distribution in the reservoir at distance from the well. However, only isotopic equilibrium exchange between water and residually trapped CO₂

can explain the isotopic shift in the water from near the wellbore. The similarity of the oxygen isotope-based result from this water sample with independent estimates based on pulsed neutron logging indicates that monitoring of oxygen isotope ratios of reservoir water in contact with free-phase CO₂ may serve as an inexpensive inherent tracer with potential to reconstruct flow-weighted averages for residual CO₂ saturation on a reservoir scale within a few days without an additional tracer.

While our most reliable sample of reservoir water in contact with residually trapped CO₂ during the Otway 2B Extension indicates the potential of using oxygen isotopes to reconstruct residual saturation in a single-well experiment, we show that the current setup of the Otway 2B Extension is not ideal to reconstruct residual trapping levels further away from the wellbore using this tracer. Further, our residual trapping estimates based on oxygen isotopes are prone to large uncertainties, which is mainly due to the small isotopic distinction of the baseline water and CO₂ values leading to small predictable shifts in $\delta^{18}\text{O}$ of reservoir water in contact with the injected CO₂. The setup of the field experiment, with two different sources of CO₂, injection of two CO₂-saturated water masses with different oxygen isotope signatures, and lower injection temperatures compared to reservoir temperatures, results in additional uncertainties in the determination of baseline conditions and in the estimation of S_{CO_2} . For future applications of this inherent tracer in an ideal single-well test, relatively simple measures can be taken to reduce these uncertainties. It should be guaranteed that baseline reservoir water and free-phase CO₂ are isotopically distinct enough to produce large shifts in the reservoir water $\delta^{18}\text{O}$ as a result of water-CO₂ oxygen isotope exchange, resulting in small uncertainties in S_{CO_2} estimates. This can be achieved by testing the isotopic signature of both oxygen sources prior to the start of an experiment. In case of a small isotopic distinction, the CO₂ or water to be injected may be isotopically spiked to further the distinction. The injection of CO₂ from a single source during the injection of pure CO₂ would increase the reliability and precision of S_{CO_2} estimates. Injection temperatures similar to reservoir conditions further away

from the wellbore would further avoid uncertainties in the determination of the oxygen isotopic enrichment factor in the reservoir, but this can be difficult to achieve in field operations.

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Figure captions

Figure 1: Water $\delta^2\text{H}$ from the Otway 2B Extension. Samples from injection periods (green (CO_2) and blue (water) bars at bottom of graph where numbers indicate tonnage) are shown as open symbols, while samples from production periods (orange bars, number = tonnage) are filled symbols. U-tube samples are shown as triangles, and bottle samples are squares. We differentiate by colour the initial water production and Phase 1.1 (black), Phase 1.2 (red), the early production phase in Phase 2 (magenta), Phase 2.1 (blue), and Phases 2.3 and 2.4 (green). Error bars show the analytical uncertainty of $\pm 2 \text{ ‰}$. The black line indicates the average of all samples (excluding the duplicate sample with much higher values from the initial water production) $\pm 1\sigma$ uncertainty. Periods of pulsed neutron logging (red bars at bottom) are shown with production data.

Figure 2: Water $\delta^{18}\text{O}$ from the Otway 2B Extension. Samples from injection periods (green (CO_2) and blue (water) bars at bottom of graph where numbers indicate tonnage) are shown as open symbols, while samples from production periods (orange bars, number = tonnage) are filled symbols. U-tube samples are shown as triangles, and bottle samples are squares. We differentiate by colour the initial water production and Phase 1.1 (black), Phase 1.2 (red), the early production phase in Phase 2 (magenta), Phase 2.1 (blue), and Phases 2.3 and 2.4 (green). Error bars show the analytical uncertainty of $\pm 0.1 \text{ ‰}$. The black line indicates the average of all samples from before the water production of the residual saturation test (prior to day 75) $\pm 1\sigma$ uncertainty. Periods of pulsed neutron logging (red bars at bottom) are shown with production data.

Figure 3: $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ in water samples from Phases 2.1, 2.3 and 2.4. Samples from injection and production periods are shown as open and filled symbols, respectively. U-tube samples are shown as triangles, and bottle samples as squares. Samples from Phase 2.1 are

in blue, from Phase 2.3 in red, from the water injection for Phase 2.4 in magenta, and for the water production of Phase 2.4 in different green colours. The thick black line indicates the local meteoric water line (LMWL) for Melbourne (Hughes and Crawford, 2012), and the black box symbolises the 1σ range of the baseline water samples prior to water production for Phase 2.4.

Figure 4: Methanol concentration (ppm) in the back-produced formation water in Phase 2.4 (open circles), compared to the fit to a simple analytical theory described in the text (solid line). The horizontal axis is the cumulative produced volume at a given time divided by the total injected volume of 67.2 t.

Tables

Table 1: Time schedule of Phase 2 of the Otway 2B Extension. Days relate to the start of the Otway 2B Extension on 3 October 2014.

Day	Phase	Description	Injection CO ₂ (t)	Injection Water (t)	Production Water (t)	Water rate (t/day)	CO ₂ rate (t/day)
63-64		Water production			75.1	50.4	
65	2.1	Water injection with noble gases and methanol		67.0		199.5	
65-67	2.1	Water production			122.2	50.4	
68		Pulsed neutron logging					
68-72	2.2	Pure CO ₂ injection	109.8				32.9
72		Pulsed neutron logging					
72-74	2.3	CO ₂ -saturated water injection	17.5	323.7		155.6	8.4
74		Pulsed neutron logging					
75	2.4	CO ₂ -saturated water injection with noble gases and methanol	3.9	67.2		155.1	9.0
75-77	2.4	Water production			128.5	49.5	

Table 2: Results of the methanol analysis for the fraction of the injected CO₂-saturated water mass for Phase 2.4 (second water mass) during the time intervals of U-tube sampling. The results are based on measured methanol concentrations in the U-tube samples and the fitted analytical model.

Day of experiment	Time	Produced water (t)	Fraction of production of second injected CO ₂ -saturated water mass
75	19:45 – 21:15	12.1	1.00
76	17:42 – 19:12	57.4	0.70 ± 0.13
77	19:20 – 20:50	110.2	0.04 ± 0.02

Table 3: Wellbore conditions for time periods of U-tube sampling during Phase 2.4. CO₂ solubilities and densities were estimated after Duan and Sun (2003). Parameters A, B and C are input parameters for Eq. (4).

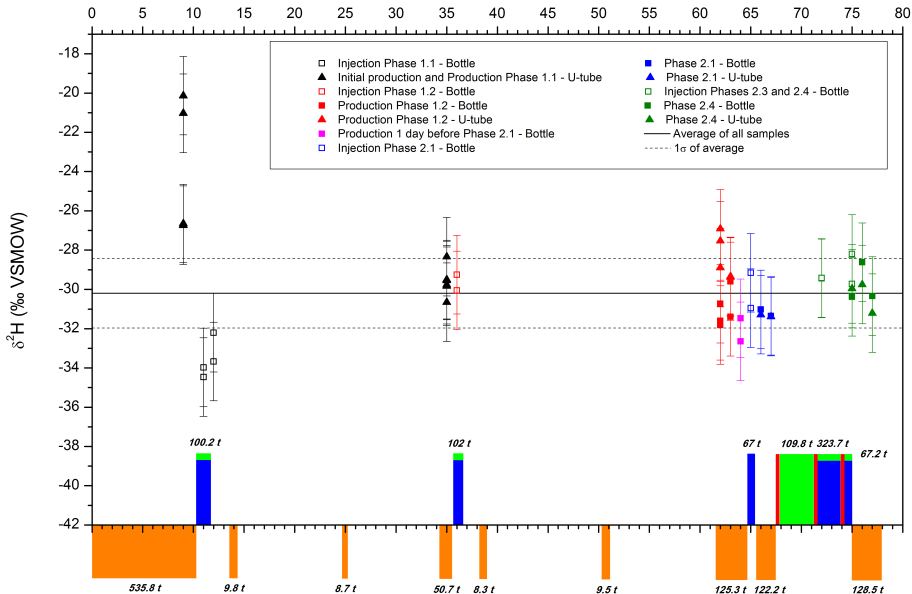
Day	Time	Average temperature (°C)	Average pressure (bar)	CO ₂ solubility (mol/kg)	CO ₂ density (g/L)	A (mol/L) [Eq. (4)]	B (mol/L) [Eq. (4)]	C (mol/L) [Eq. (4)]
75	19:45 – 21:15	42.47	139.48	1.27	744.01	33.82	2.53	55.51
76	17:42 – 19:12	45.26	139.37	1.24	720.15	32.73	2.48	55.51
77	19:20 – 20:50	47.04	139.34	1.23	704.36	32.02	2.45	55.51

Table 4: Oxygen isotope-based results of residual CO₂ saturation using Eqs. (2)-(4) for the three time intervals of U-tube sampling during Phase 2.4.

Day of experi- ment	Time	$\delta^{18}\text{O}_{\text{H}_2\text{O}}^b$ (‰ VSMOW)	ϵ [Eq. (3)] (‰)	$X_{\text{CO}_2}^o$ ¹ [Eq. (2)]	S_{CO_2} [Eq. (4)]
75	19:45 – 21:15	-5.86 ± 0.07	36.84	0.13 ± 0.06	0.14 ± 0.09
76	17:42 – 19:12	-5.96 ± 0.05	36.34	0.22 ± 0.08	0.28 ± 0.11
77	19:20 – 20:50	-6.17 ± 0.07	36.03	0.32 ± 0.13	0.42 ± 0.16

¹ Calculated using a constant $\delta^{18}\text{O}_{\text{CO}_2}$ value of +28.94 ± 0.12 ‰ and measured $\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$ values of -6.12 ± 0.10 ‰ for day 75, -6.27 ± 0.10 ‰ for day 76, and -6.46 ± 0.10 ‰ for day 77.

Day of CO2CRC Otway Stage 2B Extension



Day of CO2CRC Otway Stage 2B Extension

